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Enhanced ferroelectric photoelectrochemical properties of polycrystalline BiFeO₃ film by decorating with Ag nanoparticles

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Polycrystalline BiFeO₃ (BFO) films are fabricated on Pt/Ti/SiO₂/Si(100) substrate as photoelectrode using sol-gel method. The microstructure, optical, and photoelectrochemical (PEC) properties of the films are characterized and optimized by controlling the film thickness. Moreover, the PEC properties of the BFO films are dependent on ferroelectric polarization, which is mainly ascribed to the modulation of band structure at the BFO/electrolyte interface by the polarization. Further enhancement of PEC properties is obtained by decorating the samples with appropriate amounts of Ag nanoparticles, which is attributed to the reduced electron-hole recombination, and localized surface plasmon resonance effect of Ag nanoparticles. © 2016 AIP Publishing LLC.

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Photoelectrochemical (PEC) or photocatalytic water splitting for hydrogen and oxygen generation has been studied for several decades. To date, the most commonly used photocatalysts in PEC systems are binary transition metal oxides, such as TiO₂ and ZnO.^{1,2} However, these materials can only be activated under UV light due to their large band gap. BiFeO₃ (BFO) is a well-known multiferroic material, which exhibits robust ferroelectricity and relatively small band gap.³ Several groups have grown various nanostructures of BFO and studied their PEC properties. For example, Joshi *et al.* reported the photo-induced oxidization capability of BFO nanocubes, suggesting that it might be a promising material as photoelectrode for water photoelectrolysis.⁴ Subsequently, ordered mesoporous BFO nanoparticles (NPs) and BFO nanowires with large surface areas were prepared to improve the PEC activity.^{5,6}

However, it is difficult to control the ferroelectric polarization in powder and nanostructures and to study how the ferroelectric polarization affects PEC properties. On the other hand, it has been shown that the internal electric field originating from ferroelectric polarization in ferroelectrics offers new possibilities for exploring and controlling the photovoltaic effect.^{7,8} By analogy, appropriate control of the polarization may also significantly affect the PEC or photochemical performance of ferroelectric-based photoelectrode.^{9,10} Even though Ji *et al.* observed that the polarization only slightly affects the PEC properties of the epitaxial BFO film photoelectrode,¹¹ it could be due to the poor electric poling control in aqueous solution. Polycrystalline BFO films, due to their low cost and simple fabrication process, seem more suitable for practical applications rather than epitaxial films.¹² But the effect of ferroelectric polarization on PEC properties in these films has not been reported before.

One key issue associated with BFO as a photoelectrode material is the rapid recombination of photo-generated electrons and holes, which has to be addressed to achieve better PEC performance. An efficient way is to combine BFO with noble metal (e.g., Ag, Au, Pt) nanostructures. Since they have different work functions, Schottky barrier can be formed at the interface between metal and BFO,^{13,14} and the metal can act as a sink for photo-generated electrons, thus decreasing the recombination. Furthermore, some noble metal nanostructures can induce strong localized surface plasmon resonance (LSPR) effect,¹⁵ which can enhance the electric field near the metal/semiconductor interface, increase the photon absorption of semiconductor, and control the charge carrier generation.

Herein, polycrystalline BFO thin film photoelectrode is fabricated by sol-gel method,^{16–18} which exhibits a small band gap and suitable band positions for PEC water splitting. The effects of film thickness on the microstructure, photoabsorption, and PEC performance are studied in detail. Most importantly, we observe an effective tuning of the PEC properties by the ferroelectric polarization of BFO. In addition, the PEC performance is further enhanced by decorating BFO with Ag NPs of appropriate amount. This discovery provides an active path to the design of ferroelectric oxides-based photoelectrode for PEC water splitting.

Bi(NO₃)₃·5H₂O and Fe(NO₃)₃·9H₂O were dissolved in 2-methoxyethanol and stabilized by adding citric acid. The solution was spin-coated onto Pt/Ti/SiO₂/Si(100) substrate for PEC measurement and onto FTO substrate for optical absorption measurement. The wet films were dried at 200 °C in air for 2 min, followed by 400 °C for 5 min. This coating process was repeated several times to achieve the desired film thickness. Finally, the films were annealed at 640 °C in O₂ for 2 h.

A three electrodes setup was adopted to decorate Ag NPs onto the BFO films. The BFO films act as the working electrode, a Pt wire as the counter electrode, and an Ag/AgCl electrode as the reference electrode. An aqueous solution of

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10 mM AgNO₃ and 100 mM NaNO₃ was used as electrolyte. Then, a pulsed current of 10 mA/cm² with an alternating 0.1 s on time and 0.3 s off time was applied. To investigate the effect of the Ag amount on the properties of the BFO films, the electrodeposition time was controlled at 0, 10, 15, and 25 s. The samples obtained were denoted as BFO, 10s-Ag/BFO, 15s-Ag/BFO, and 25s-Ag/BFO, respectively.

The structure of the films was analyzed using an X-ray diffraction (XRD) diffractometer (Rigaku D/MAX 3 C). The surface morphology of the films was measured using a scanning electron microscope (SEM, HITACHI S-4700). Piezoresponse force microscopy (PFM) measurements were carried out on a commercial atomic force microscope (MFP-3D, Asylum Research) using Pt/Ir-coated tips. The optical absorption spectra of the films were measured using a UV/Vis/NIR spectrometer (Perkin Elmer Lambda 750). Photoluminescence (PL) spectra were measured using an excitation wavelength of 260 nm on a spectrofluorometer (Jasco FP-6500). The PEC properties were measured in a conventional three-electrode setup using an electrochemical analyzer (CHI-600D). The films, a Pt wire, and an Ag/AgCl electrode were used as the working, the counter, and the reference electrodes, respectively. 0.1 M Na₂SO₄ aqueous solution was used as the electrolyte. The light source was a 300 W Xe lamp with tunable light intensity, calibrated using a Newport 1918-C photometer. Mott-Schottky measurements were measured in 0.1 M Na₂SO₄ in dark at a frequency of 1 kHz and scan rate of 10 mV/s. The Nyquist plot was obtained using an AC voltage of 10 mV with a frequency range of 0.01 Hz to 10 MHz.

Figure 1(a) shows the XRD patterns of the BFO films with different thicknesses. All the films have a well-crystallized pure BFO phase (JSPDS file No. 21-1272). Moreover, the intensity of BFO diffraction peaks increases with increasing film thickness, indicating larger grains, which is confirmed by the SEM images shown in Figures 1(b)–1(e). The micrographs indicate well-grown polycrystalline films

with average grain size varying from about 70 to 150 nm. Figure 1(f) shows the out-of-plane PFM phase image of a 200 nm BFO film. Stable ferroelectric domains with opposite polarities can be written by applying a voltage to the AFM tip during scan (The topographies of the corresponding sample before and after PFM measurement are shown in Figure S1, which confirm that the observed color contrast is not derived from the surface damage during the PFM measurement.).¹⁹ The PFM hysteresis loop of the corresponding film also demonstrates the ferroelectric nature of it (Figure 2(g)). The local coercive voltages are about +5.0 and −4.0 V, as indicated by the minima of the amplitude loop.

Figure 2(a) shows the UV-vis absorption spectra of the BFO films with different thicknesses. All the curves show a broad absorption band between 400 and 550 nm, which indicates that BFO thin films can absorb considerable amount of visible light, implying their potential application as visible-light driven PEC photoelectrode material. The corresponding energy band gaps can be estimated from the $(\alpha h\nu)^2 - (h\nu)$ plot by extrapolating the linear portion of $(\alpha h\nu)^2$ to zero, where α , h , and ν are absorption coefficient, Planck constant, and light frequency, respectively. As shown in the inset of Figure 2(a), the energy band gap of the BFO film decreases from about 2.46 to 2.32 eV with increasing film thickness. Such phenomenon can be attributed to the improvement of the crystallization as suggested by XRD pattern and SEM images. It should be noted that the values of the band gaps in our samples are lower than those reported in the epitaxial BFO films (~2.7 eV).^{20–22} One possible mechanism for such difference is the defect states due to oxygen vacancies. In stoichiometric BFO, the bandgap is between the O 2*p* and Fe 3*d* levels. For polycrystalline BFO films, the oxygen vacancies are more easily formed, which can lower the adjacent Fe 3*d* levels, resulting in sub-band gap defect states.²³ The theoretical calculation suggests that defect states due to oxygen vacancies lead to transitions at ~0.3 eV below the band gap.²⁴ Thus, the existence of the defect states could be the reason of having the

FIG. 1. (a) XRD patterns of the BFO films with different thicknesses. The SEM micrographs of the BFO films with different thicknesses: (b) 160 nm; (c) 200 nm; (d) 240 nm; and (e) 280 nm. (f) The amplitude image of the out-of-plane piezoelectric response of the 200 nm BFO films. (g) Local PFM hysteresis loops of the 200 nm BFO films: top, phase signal; bottom, amplitude signal.

FIG. 2. (a) The UV-vis absorption of the BFO films with different thicknesses, the inset is the optical band gap of the corresponding samples. (b) The UV-vis absorption spectra of the different Ag/BFO samples, the inset is the UV-vis absorption spectra of Ag NPs deposited on FTO substrate for 15 s.

lower band gap in our polycrystalline films. Figure 2(b) shows the UV-vis absorption spectra of the pure BFO and Ag/BFO films, which will be discussed in detail later.

Figure 3(a) shows the amperometric I - t curves of the BFO thin film photoelectrodes with different thicknesses. The photocurrent appears promptly after the light is turned on, and then reaches a steady state. It can be seen that the short-circuit photocurrent densities of all the films are negative values, typical of p -type semiconductors.²⁵ With increasing film thickness, the photocurrent density initially increases to a maximal value and then decreases again, which indicates that the photocurrent is strongly correlated with the thickness of BFO films. The optimal BFO film thickness is 200 nm, and the photocurrent density is $15 \mu\text{A}/\text{cm}^2$, which is comparable to that of epitaxial BFO ($10 \mu\text{A}/\text{cm}^2$ at 0.64 V vs. Ag/AgCl).¹¹ The initial increase of photocurrent density can be ascribed to the increased amount of photoactive material, which enhances the light absorption as well as the total number of photoexcited carriers.²⁶ Once the BFO film thickness reaches a certain threshold, charge carrier recombination becomes increasingly important, since the very short carrier diffusion length effectively limits the ability to remove charges from the semiconductor.

In order to estimate the conduction and valence band edges of BFO, Mott-Schottky measurements are performed on a 200 nm film, and the capacitance (C) as a function of the applied photoelectrode potential (V) is shown in Figure 3(b).

The negative slope of $1/C^2$ versus V again demonstrates p -type characteristic of our BFO films,²⁷ which is consistent with the negative photocurrent. The linear region can be extrapolated to obtain the x-axis intercept ($V_{fb} = 1.22 \text{ V}$ versus Ag/AgCl or $+2.26 \text{ V}$ versus normal hydrogen electrode (NHE) at $\text{pH} = 6.8$). For p -type semiconductor, the valence band maxima (VBM) can be calculated from the flat-band potential (V_{fb}) following the equation, $E_V = V_{fb} + kT \ln(N_A/N_V) - kT/e^2$,²⁸ where N_A is the acceptor concentration, N_V is the effective density of states (typically $\sim 10^{19}$) at the valence band edge, k is the Boltzmann constant, and T is temperature. The acceptor density, N_A , from the Mott-Schottky plot is found to be $8.5 \times 10^{18} \text{ cm}^{-3}$. This yields a VBM of $+2.68 \text{ V}$ versus NHE ($\text{pH} = 6.8$). Based upon this value and the band gap of BFO, a band diagram is constructed (Figure 3(c)). The VBM of BFO is more positive than the ($\text{O}_2/\text{H}_2\text{O}$) redox couple, indicating BFO favors oxidation reactions, i.e., oxygen evolution.^{4,29}

To study the effect of the ferroelectric polarization on the PEC properties, the 200 nm BFO films were macroscopically poled in an electrochemical cell containing three electrodes and aqueous electrolyte ($0.1 \text{ M Na}_2\text{SO}_4$).³⁰ Potentials of $+8 \text{ V}$ and -8 V were applied on the Ag/AgCl electrode, and the polarization pointing away (towards) the substrate is defined as upward (downward) polarization, abbreviated as P_{up} (P_{down}). During the poling procedure, the current was kept below 1 mA . As shown in Figure 3(d), the photocurrent density of BFO is strongly depended on the polarization states. The onset

FIG. 3. (a) Photocurrent densities versus time for the BFO films with different thicknesses; (b) Mott-Schottky plot (inverse capacitance squared ($1/C^2$) versus potential (V)) for the 200 nm BFO films; (c) Schematic illustration for the calculated energy level diagram of BFO; and (d) Linear sweep voltammetry curves of the 200 nm BFO films with different ferroelectric polarizations.

potential is 0.08 V for the films with the upward polarization, while it is -0.12 V for the downward polarization. Moreover, the short-circuit photocurrent density with downward polarization is larger than that with upward polarization.

On the basis of our observations, the effect of different polarization states in BFO is depicted in Figure 4. It has been noted that the large polarization charge can induce a significant change in the band structure near the electrode/ferroelectric interface.³¹ Moreover, in the case of our BFO photoelectrode, the objective is to realize water oxidation at the photoelectrode/electrolyte interface, which is desirable to drive the hole accumulation at the surface. Poling the polarization downward will induce the upward band bending with built-in field E_{bi} on the electrolyte/BFO surface, which attracts holes from the bulk to the surface, thus enhancing the PEC activity. When the polarization of BFO is reversed, the E_{bi} direction is also reversed as shown in Figure 4(b), which is unfavorable for the hole accumulation and reduces the PEC activity. Such result is consistent with previous studies where it has been demonstrated that photooxidation reactions occur preferably on downward polarized ferroelectric domains.^{32,33}

To further increase the PEC performance of the BFO films, Ag NPs are deposited on the surfaces. Figure S2(a) shows the SEM image of the 15s-Ag/BFO film. Closer observation reveals that Ag NPs are dispersed onto the surface of BFO, as indicated by the arrows. In addition, the typical energy dispersive X-ray spectroscopy (EDX) spectrum obtained from the corresponding sample confirms the presence of Ag, Bi, Fe, and O (Figure S2(b)).¹⁹ Figure 2(b) shows the UV-vis absorption spectra of the pure BFO and Ag/BFO films. A red shift of absorption edge and enhancement of light absorption can be observed for Ag/BFO samples, which is due to the LSPR effect of Ag NPs.³⁴ The peak of Ag NPs' plasmon resonance absorbance (inset of Figure 2(b)) cannot be clearly observed in the spectra, since it nearly overlaps with the absorption edge of BFO. In addition, by increasing the Ag NPs electrodeposition time, the absorption of the corresponding samples is increased.

The photocurrent densities of the pure BFO and Ag/BFO photoelectrodes are shown in Figure 5(a). Upon illumination, all the Ag decorated BFO samples exhibit higher photocurrent intensities than that of the pure BFO sample. In addition, it is

found that the effect of Ag NPs has an optimum deposition time window. The highest photocurrent density value observed in the 15s-Ag/BFO film is about $35 \mu\text{A}/\text{cm}^2$, which is almost twice that of the pure BFO film. When the amount of Ag NPs is low, the photocurrent density increases with the increment of Ag loading amount because the LSPR effect enhances with the increment of Ag amount. However, the high coverage of Ag NPs amount reduces the surface area of BFO in direct contact with the electrolyte, and the superfluous Ag NPs may also act as recombination sites, resulting in a decrease in photocurrent density. Figure 5(b) shows the corresponding photocurrent density of 15s-Ag/BFO sample during a 2 h measurement, which implies the stability of the photoelectrode.

EIS (electrochemical impedance spectroscopy) is commonly used to investigate the charge transfer resistance and the separation efficiency of photogenerated electrons and holes.³⁵ To reveal the kinetics of charge transfer in the Ag/BFO photoelectrode, the EIS measurement is carried out without illumination. Figure 5(c) shows the Nyquist plots of the pure BFO and Ag/BFO photoelectrodes. Obviously, the resistances of Ag/BFO photoelectrodes are smaller than that of the BFO photoelectrode, the 15s-Ag/BFO sample has the smallest resistance. Such results indicate that Ag NPs can actually enhance the electron mobility by suppressing the recombination of photogenerated electrons and holes in the composite photoelectrodes. More, this conclusion can be further confirmed by the corresponding PL measurement, as shown in Figure 5(d). It is known that a lower PL peak intensity implies higher efficiency in the separation of photogenerated charge carriers.³⁶ One emission peak is detected at around 540 nm in all the samples, which is also reported in previous report.⁶ Again, the pure BFO sample has the highest PL intensity, while the 15s-Ag/BFO sample has the lowest PL intensity, which is consistent with the EIS result.

The enhanced PEC properties of Ag NPs decorated BFO photoelectrode can be explained as follow: When Ag NPs and BFO are in contact, free electrons will redistribute across the interfaces to realign the Fermi levels of the two systems until equilibrium state is achieved. So Schottky barriers are formed between Ag and BFO, and the Ag NPs act as electron traps aiding the electron-hole separation. Meanwhile, a local electric field enhancement can be achieved at the Ag/BFO interfaces

FIG. 4. Schematic of the energy band diagrams and operational principle of the PEC properties for the BFO film (a) downward and (b) upward polarization states of BFO. E_F , E_V , and E_C represent Fermi level, valence band, and conduction band of BFO, respectively. The corresponding top schematic shows the directions of the poling electric field and the photocurrent.

FIG. 5. (a) Photocurrent densities versus time for the Ag/BFO and pure BFO films; (b) The stability of the 15s-Ag/BFO films; (c) EIS Nyquist plots of the corresponding samples; and (d) PL spectra of the corresponding samples.

due to LSPR excitation, which amplify the light absorption of BFO and generate more electron-hole pairs. Therefore, the synergistic effect of Schottky barriers and LSPR can improve the PEC properties of the Ag/BFO sample.

In summary, polycrystalline BFO thin film photoelectrodes were synthesized by sol-gel method. The effects of film thickness on the microstructure, optical, and PEC properties of the BFO photoelectrodes were investigated in detail. The photocurrent density in downward polarized BFO is larger than that in upward polarized BFO, as a result of the modulation of the band structure. The PEC properties of BFO thin films can be further enhanced by decorating Ag NPs. The 15s-Ag/BFO photoelectrode has the maximum photocurrent density, which is almost twice that of the pure BFO photoelectrode. Such enhancement can be attributed to the improved separation efficiency of the photogenerated electron-hole pairs and LSPR effect of Ag NPs.

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¹A. Fujishima and K. Honda, *Nature* **238**, 37 (1972).

²M. G. Walter, E. L. Warren, J. R. McKone, S. W. Boettcher, Q. X. Mi, E. A. Santori, and N. S. Lewis, *Chem. Rev.* **110**, 6446 (2010).

³T. Choi, S. Lee, Y. J. Choi, V. Kiryukhin, and S. W. Cheong, *Science* **324**, 63 (2009).

⁴U. A. Joshi, J. S. Jang, P. H. Borse, and J. S. Lee, *Appl. Phys. Lett.* **92**, 242106 (2008).

⁵I. Papadas, J. A. Christodoulides, G. Kioseoglou, and G. S. Armatas, *J. Mater. Chem. A* **3**, 1587 (2015).

⁶S. Li, J. M. Zhang, M. G. Kibria, Z. Mi, M. Chaker, D. L. Ma, R. Nechache, and F. Rosei, *Chem. Commun.* **49**, 5856 (2013).

⁷S. Y. Yang, L. W. Martin, S. J. Byrnes, T. E. Conry, S. R. Basu, D. Paron, L. Reichertz, J. Ihlefeld, C. Adamo, A. Melville, Y. H. Chu, C. H. Yang, J. L. Musfeldt, D. G. Schlom, J. W. Ager, and R. Ramesh, *Appl. Phys. Lett.* **95**, 062909 (2009).

⁸D. Lee, S. H. Baek, T. H. Kim, J. G. Yoon, C. M. Folkman, C. B. Eom, and T. W. Noh, *Phys. Rev. B* **84**, 125305 (2011).

⁹D. Steve, M. J. Paul, and E. G. Diego, *J. Am. Chem. Soc.* **129**, 8724 (2007).

¹⁰D. W. Cao, Z. J. Wang, Nasori, L. Y. Wen, Y. Mi, and Y. Lei, *Angew. Chem. Int. Ed.* **53**, 11027 (2014).

¹¹W. Ji, K. Yao, Y. F. Lim, Y. C. Liang, and A. Suwardi, *Appl. Phys. Lett.* **103**, 062901 (2013).

¹²X. Y. Chen, T. Yu, F. Gao, H. T. Zhang, L. F. Liu, Y. M. Wang, Z. S. Li, and Z. G. Zou, *Appl. Phys. Lett.* **91**, 022114 (2007).

¹³H. A. Atwater and A. Polman, *Nat. Mater.* **9**, 205 (2010).

¹⁴A. Takai and P. V. Kamat, *ACS Nano* **5**, 7369 (2011).

¹⁵S. Linic, P. Christopher, and D. B. Ingram, *Nat. Mater.* **10**, 911 (2011).

¹⁶Y. Wang, Q. H. Jiang, H. C. He, and C. W. Nan, *Appl. Phys. Lett.* **88**, 142503 (2006).

¹⁷S. Iakovlev, C. H. Solterbeck, M. Kuhnke, and M. Es-Souni, *J. Appl. Phys.* **97**, 094901 (2005).

¹⁸S. K. Singh, H. Ishiwara, and K. Maruyama, *Appl. Phys. Lett.* **88**, 262908 (2006).

¹⁹See supplementary material at <http://dx.doi.org/10.1063/1.4939747> for the AFM topographic image of the 200 nm BFO films, SEM image, and EDX spectrum of the 15s-Ag/BFO films.

²⁰A. Kumar, R. C. Rai, N. J. Podraza, S. Denev, M. Ramirez, Y. H. Chu, L. W. Martin, J. Ihlefeld, T. Heeg, J. Schubert, D. G. Schlom, J. Orenstein, R. Ramesh, R. W. Collins, J. L. Musfeldt, and V. Gopalan, *Appl. Phys. Lett.* **92**, 121915 (2008).

²¹J. F. Ihlefeld, N. J. Podraza, Z. K. Liu, R. C. Rai, X. Xu, T. Heeg, Y. B. Chen, J. Li, R. W. Collins, J. L. Musfeldt, X. Q. Pan, J. Schubert, R. Ramesh, and D. G. Schlom, *Appl. Phys. Lett.* **92**, 142908 (2008).

²²S. R. Basu, L. W. Martin, Y. H. Chu, M. Gajek, R. Ramesh, R. C. Rai, X. Xu, and J. L. Musfeldt, *Appl. Phys. Lett.* **92**, 091905 (2008).

²³A. J. Hauser, J. Zhang, L. Mier, R. A. Ricciardo, P. M. Woodward, T. L. Gustafson, L. J. Brillson, and F. Y. Zhang, *Appl. Phys. Lett.* **92**, 222901 (2008).

²⁴S. Ju and T. Y. Cai, *Appl. Phys. Lett.* **95**, 231906 (2009).

²⁵S. Li, B. Alotaibi, W. Huang, Z. Mi, N. Serpone, R. Nechache, and F. Rosei, *Small* **11**, 4018 (2015).

²⁶G. M. Wang, Y. C. Ling, D. A. Wheeler, K. E. N. George, K. Horsley, C. Heske, J. Z. Zhang, and Y. Li, *Nano Lett.* **11**, 3503 (2011).

²⁷F. P. Koffyberg and F. A. Benko, *J. Appl. Phys.* **53**, 1173 (1982).

²⁸P. P. Sahoo, B. Zoellner, and P. A. Muggard, *J. Mater. Chem. A* **3**, 4501 (2015).

²⁹S. J. A. Moniz, R. Quesada-Cabrera, C. S. Blackman, J. W. Tang, P. Southern, P. M. Weaver, and C. J. Carmalt, *J. Mater. Chem. A* **2**, 2922 (2014).

³⁰M. Zhang, C. X. Jiang, W. Dong, F. G. Zheng, L. Fang, X. D. Su, and M. R. Shen, *Appl. Phys. Lett.* **103**, 102902 (2013).

³¹L. Fang, L. You, Y. Zhou, P. Ren, Z. S. Lim, and J. Wang, *Appl. Phys. Lett.* **104**, 142903 (2014).

³²J. Chen, H. D. Lu, H. J. Liu, Y. H. Chu, S. Dunn, K. Ostrikov, A. Gruverman, and N. Valanoor, *Appl. Phys. Lett.* **102**, 182904 (2013).

³³M. Rioult, S. Datta, D. Stanesco, S. Stanesco, R. Belkhou, F. Maccherozzi, H. Magnan, and A. Barbier, *Appl. Phys. Lett.* **107**, 103901 (2015).

³⁴Z. Y. Chen, L. Fang, W. Dong, F. G. Zheng, M. R. Shen, and J. L. Wang, *J. Mater. Chem. A* **2**, 824 (2014).

³⁵B. Y. Chang and S. M. Park, *Annu. Rev. Anal. Chem.* **3**, 207 (2010).

³⁶J. G. Yu, H. G. Yu, B. Cheng, X. J. Zhao, J. C. Yu, and W. K. Ho, *J. Phys. Chem. B* **107**, 13871 (2003).